

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B29B 11/16, 15/12	A1	(11) International Publication Number: WO 98/30374 (43) International Publication Date: 16 July 1998 (16.07.98)
(21) International Application Number: PCT/US97/00898 (22) International Filing Date: 8 January 1997 (08.01.97) (71) Applicants: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US). DOW-UNITED TECHNOLOGIES COMPOSITE PRODUCTS, INC. [US/US]; 15 Sterling Drive, Wallingford, CT 06492-1843 (US). (72) Inventors: LOPEZ, Leonardo, C.; 4200 Brambleridge Lane, Midland, MI 48640 (US). PELLETIER, Ronald, R.; 1820 Rapanos Drive, Midland, MI 48642 (US). FORSYTHE, Paul, D.; 6 Todds Mill Circle, Madison, CT 06443 (US). (74) Agent: DAMOCLES, Nemia, C.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PROCESS FOR PREPARING PREFORMS AND MOLDED ARTICLES (57) Abstract A process for making an article made of a fiber-reinforced composite material comprises: (1) preparing a preform by (i) coating one or more reinforcement fibers in the form of a continuous filament or tow with an aqueous dispersion of a tackifier, (ii) winding the coated filament or tow, while still wet, onto a mandrel having the shape of a desired article, (iii) heating the coated reinforcement fibers to a temperature and for a time sufficient to remove the water present and to partially melt the tackifier on the surface of the reinforcement fibers, and (iv) removing the mandrel from the filament-wound reinforcement fibers to provide a preform; and (2) subjecting the preform to a resin transfer molding process to provide an article comprising a fiber-reinforced composite material.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

PROCESS FOR PREPARING PREFORMS AND MOLDED ARTICLES

This invention relates to methods for preparing preforms useful in resin transfer molding processes and preforms prepared thereby.

5 Processes for preparing preforms are well known. These processes employ conventional powder coating techniques to apply a tackifier onto the surface of a reinforcement fiber. In such processes, a tackifier, in powder form, is distributed and fused on the surface of the reinforcement fiber. At the low tackifier concentrations utilized in preforming, it is difficult to obtain a uniform tackifier distribution with powder coating
10 techniques due to the electrostatic charge generated on fine powders during the application operations. Uniform distribution of the tackifier is also difficult to achieve because of the high viscosity of the melted tackifier. Also, such processes are very costly and have the potential of causing excessive break-up of the reinforcement fibers. Furthermore, the large particle size of the tackifier typically used in powder coating methods can cause compaction problems in the
15 preform, making it difficult to obtain the preform thickness required for subsequent molding processes. Other known processes comprise dissolving the tackifier in a suitable solvent, applying the tackifier solution onto the surface of the reinforcement fiber and then drying the reinforcement fiber containing the tackifier solution to evaporate the solvent. However, the tackifier solution leaves a continuous film coating on the surface of the reinforcement fiber
20 which becomes stiff upon evaporation of the solvent which, in turn, makes the coated reinforcement fiber difficult to make into a preform.

The above prior art processes for preparing preforms are, in general, very slow and are, therefore, not suitable for high volume production of articles. Also, preforms made by these processes are typically not suitable for use in Resin Transfer Molding (RTM) because they
25 usually do not properly fit into the mold. Current "state of the art" of preform technology is one of the limiting factors preventing RTM from being used in high volume applications such as, for example, the production of golf club shafts.

Golf club shafts made of fiber-reinforced composite materials are known in the art and are described, for example, in U.S. Patent 3,313,541. The process described in this
30 patent for making the golf club shafts involves many steps and is very labor intensive.

Attempts have been made in the past to make golf club shafts by resin transfer molding dry filament-wound preforms, but were unsuccessful because the preforms do not fit properly into the mold, resulting in high localized fiber volumes.

It would be desirable to provide a process for preparing preforms which is simple
35 and suitable for use in high volume applications, such as the production of golf club shafts.

In a first aspect, this invention is a process for preparing preforms which comprises the sequential steps of (1) coating reinforcement fibers, in the form of continuous filaments or tows, with an aqueous dispersion of a tackifier, (2) winding the coated filaments or tows, while

still wet, onto a mandrel having the shape of a desired article, (3) heating the coated reinforcement fibers to a temperature and for a time sufficient to remove the water present and to partially melt the tackifier on the surface of the reinforcement fibers and (4) removing the mandrel from the wound reinforcement fibers to provide a preform.

5 In a second aspect, this invention is a process for preparing preforms which comprises the sequential steps of (1) coating reinforcement fibers, in the form of continuous filaments or tows, with a tackifier dissolved in an organic solvent (tackifier solution), (2) winding the coated filaments or tows, while still wet, onto a mandrel having the shape of a desired article, (3) heating the coated reinforcement fibers to a temperature and for a time
10 sufficient to evaporate the solvent and to melt the tackifier on the surface of the reinforcement fibers and (4) removing the mandrel from the wound reinforcement fibers to provide a preform.

In a third aspect, this invention is a process for preparing preforms which comprises the sequential steps of (1) coating reinforcement fibers, in the form of continuous
15 filaments or tows, with an aqueous dispersion of a tackifier, (2) heating the coated reinforcement fibers to a temperature and for a time sufficient to remove the water present and to partially melt the tackifier on the surface of the reinforcement fibers, (3) winding the coated filaments or tows onto a mandrel having the shape of a desired article and (4) removing the mandrel from the wound reinforcement fibers to provide a preform.

20 In a fourth aspect, this invention is a process for making an article made of a fiber-reinforced composite material which comprises:

(1) preparing a preform by (i) coating reinforcement fibers with an aqueous dispersion of a tackifier, (ii) forming the coated reinforcement fibers into a preform having the shape of a desired article and (iii) heating the coated reinforcement fibers to a temperature
25 and for a time sufficient to remove the water present and to partially melt the tackifier on the surface of the reinforcement fibers; and

(2) subjecting the preform to a resin transfer molding process to provide an article comprising a fiber-reinforced composite material.

30 In a fifth aspect, this invention is a process for making an article made of a fiber-reinforced composite material which comprises:

(1) preparing a preform by (i) coating one or more reinforcement fibers in the form of a continuous filament or tow with an aqueous dispersion of a tackifier, (ii) winding the coated filament or tow, while still wet, onto a mandrel having the shape of a desired article, (iii) heating the coated reinforcement fibers to a temperature and for a time sufficient to
35 remove the water present and to partially melt the tackifier on the surface of the reinforcement fibers and (iv) removing the mandrel from the filament-wound reinforcement fibers to provide a preform; and

(2) subjecting the preform to a resin transfer molding process to provide an article comprising a fiber-reinforced composite material.

In a sixth aspect, this invention is a process for making an article made of a fiber-reinforced composite material which comprises:

- 5 (1) preparing a preform by (i) coating one or more reinforcement fibers in the form of a continuous filament or tow with a tackifier dissolved in an organic solvent (tackifier solution), (ii) winding the coated filament or tow, while still wet, onto a mandrel having the shape of a desired article, (iii) heating the coated reinforcement fibers to a temperature and for a time sufficient to evaporate the solvent and to melt the tackifier on the surface of the
10 reinforcement fibers and (iv) removing the mandrel from the filament-wound reinforcement fibers to provide a preform; and

(2) subjecting the preform to a resin transfer molding process to provide an article comprising a fiber-reinforced composite material.

15 As used herein, the term "desired article" refers to the article made from the preform.

Fiber-reinforced composites are well known in the art and are described, for example, in Kirk-Othmer Ency. Chem., Tech. Supp., "Composites, High Performance," pp. 260-281 (J. Wiley & Sons, 1984). A composite typically comprises a plurality of fibers (reinforcement
20 fibers) embedded in a plastic (the matrix). Typically, the fibers give strength and/or stiffness to the composite, and the matrix maintains fiber orientations and spacings, transmits shear loads between layers of fibers so that they resist bending and compression and protects the fiber from surface damage.

Reinforcement fibers are also well known in the art. See, for example, E. G. Kirk-Othmer, Encyclopedia of Chemical Technology-Supplement, "Composites, High Performance,"
25 pp. 260-281 (J. Wiley & Sons, 1984). Well-known reinforcement fibers include quartz, aramid, boron, glass, carbon, or gel-spun polyethylene fibers. The fibers can be unidirectional or multidirectional. They can be monofilament fibers, multifilament fibers, ribbons, strips, a plurality of any one or combinations thereof, having regular or irregular cross-section. They may be in the form of woven or non-woven mats or fabric, or in the form of random short
30 fibers. They may also be in the form of fibrous tows or tapes.

Generally, the aqueous tackifier dispersion comprises a tackifier, water and a surfactant which serves as a dispersing or suspending agent. The aqueous tackifier dispersion can be prepared by dispersing the tackifier (usually in the form of a solution in an organic solvent) in water using a suitable surfactant and removing the organic solvent. A suitable
35 process for preparing the aqueous tackifier dispersion is described in U.S. Patent 3,726,824. If the tackifier is in the form of a solid resin, the aqueous tackifier dispersion can be prepared by dissolving the tackifier in a suitable organic solvent, contacting the tackifier solution with

water and surfactant with agitation and then removing the solvent by any conventional means such as, for example, rotary evaporation or vacuum distillation.

Organic solvents which can be employed in the practice of the present invention in preparing the tackifier solution include, for example, acetone, methylene chloride, methyl
5 ethyl ketone, ethyl acetate, isopropyl acetate, propylene oxide, dioxane, tetrahydrofuran and mixtures thereof. Preferred solvents are acetone, methylene chloride and tetrahydrofuran. More preferred solvents are acetone, and methylene chloride. The most preferred solvent is methylene chloride.

As used herein, the term "tackifier" means a resin that exhibits thermoplastic
10 properties, such as resins possessing a glass-transition temperature and/or a melting point below the temperature that cures the resin. The tackifier can also be a thermoplastic-like resin. A "thermoplastic-like" resin is a thermosetting resin that has a glass-transition temperature and/or a melting point below the curing temperature of the resin, or a resin that can partially cure at the preforming temperature so that it adheres to the reinforcement but maintains
15 thermoplastic-like properties.

Tackifiers which can be employed in the practice of the present invention in making the preforms are those resinous compounds which are also compatible with the compounds used in subsequent molding processes where the preforms are employed. Suitable tackifiers include, for example, epoxy resins, vinyl ester resins, unsaturated polyester resins,
20 polyimides, bismaleimides, polycyanate ester resins, benzocyclobutene resins and combinations thereof.

Preferred epoxy resins include the polyglycidyl ethers of polyhydric phenols (compounds having an average of more than one phenolic hydroxyl group per molecule) such as, for example, the diglycidyl ethers of biphenol, bisphenols, hydrocarbyl-substituted
25 biphenol, hydrocarbyl-substituted bisphenols, phenol- or hydrocarbyl-substituted bisphenol-aldehyde novolac resins, unsaturated hydrocarbon-phenol or hydrocarbyl-substituted phenol resins and mixtures thereof. More preferred epoxy resins are the diglycidyl ethers of bisphenol A having an epoxide equivalent weight of from 650 to 750. Most preferred is a diglycidyl ether of bisphenol A having a melting point of 55°C to 60°C, and an epoxide equivalent weight of
30 675 to 750.

Preferred vinyl ester resins include, for example, the acrylates and methacrylates of polyglycidyl ethers of compounds having an average of more than one phenolic hydroxyl group per molecule. More preferred vinyl ester resins are the reaction products of the diglycidyl ether of bisphenol A and acrylic or methacrylic acid, said reaction product having a
35 number average molecular weight of from 800 to 1400. Most preferred vinyl ester resin is the reaction product of bisphenol A and acrylic acid having a number average molecular weight of from 950 to 1250.

Preferred unsaturated polyester resins include, for example, the reaction products of fumaric acid, and propoxylated or ethoxylated bisphenol A, the reaction products of maleic anhydride and ethoxylated or propoxylated bisphenol A and the pentaerythritol ester of tall oil resin. More preferred unsaturated polyester resins are the reaction products of maleic anhydride and ethoxylated or propoxylated bisphenol A and the pentaerythritol ester of tall oil resin. The most preferred unsaturated polyester resin is the pentaerythritol ester of tall oil resin, commercially available from Union Camp Company as UNI-TAC R100.

Preferred polyimide and bismaleimide resins are described in Stenzenberger, "Recent Advances in Thermosetting Polyimides," 20, British Polymer Journal, pp. 383-396 (1988). More preferred bismaleimide resins are 4,4'-bismaleimido-diphenylmethane, 1,4-bismaleimido-2-methylbenzene and mixtures thereof; modified and partially advanced modified bismaleimide resins containing Diels-Alder comonomers; and a partially advanced bismaleimide based on 4,4'-bismaleimido-diphenylmethane and alkylphenyl compounds or aromatic amines. Examples of suitable Diels-Alder comonomers include styrene and styrene derivatives, bis(propenylphenoxy) compounds, 4,4'-bis(propenylphenoxy)sulfones, 4,4'-bis(propenylphenoxy)benzophenones and 4,4'-1-(1-methyl ethylidene)-bis(2-(2-propenyl)-phenol). Examples of commercially available modified bismaleimides based on 4,4'-bismaleimidodiphenylmethane and an alkylphenyl compound, such as diallylbisphenol A, are Matrimid™ 5292A and Matrimid™ 5292B from Ciba-Geigy Corporation. Other more preferred bismaleimides include Michael addition copolymers of bismaleimide and aromatic diamines, such as 4,4'-bismaleimidodiphenylmethane/-4,4'-diaminodiphenylmethane. Still other more preferred bismaleimides are higher molecular weight bismaleimides produced by advancement reactions of the aforementioned bismaleimide resins. Most preferred bismaleimide resins are those based on 4,4'-bismaleimidodiphenylmethane and 1,4-bismaleimido-2-methylbenzene.

The concentration of the tackifier in the dispersion will vary depending on the particular tackifier used, the form of the reinforcement fiber, the particular coating method used and the application in which the coated reinforcement fiber will be used. In general, the aqueous dispersion has a resin solids content of at least about 0.1 weight percent, preferably at least about 1 weight percent, more preferably at least about 3 weight percent and most preferably at least about 29 weight percent, based on the weight of the dispersion. In general, the aqueous dispersion has a resin solids content of not greater than about 70 weight percent, preferably not greater than about 68 weight percent, more preferably not greater than about 65 weight percent and most preferably not greater than about 60 weight percent, based on the weight of the dispersion.

An aqueous dispersion typically consists of finely divided particles distributed throughout an aqueous medium. The particle size distribution of the dispersed particles is seldom uniform in such a dispersion, but the degree of uniformity can be improved by proper selection of surfactant and controlled conditions of the dispersion process.

Dispersing agents which can be employed in the practice of the present invention in preparing the aqueous tackifier dispersion are any dispersing agents known in the art which can aid the formation and stabilization of the tackifier particles in the aqueous medium. Anionic, cationic and nonionic surfactants which emulsify the resins in water are useful as dispersing agents in this invention. Anionic and cationic surfactants are preferred. Saturated and unsaturated C₁₂₋₃₀ carboxylic acids or salts, sulfated alkylphenoxypoly(ethyleneoxy)ethanols and alkali or ammonium salts thereof and dialkyl esters of alkali sulfosuccinic acid are more preferred. An example of an alkali salt of a dialkyl ester of sulfosuccinic acid is the dioctyl ester of sodium sulfosuccinic acid commercially available from American Cyanamid as Aerosol™ OT. Saturated or unsaturated C₁₂₋₃₀ carboxylic acids or salts thereof are more preferred. Alkali metals and ammonium ions are the preferred counterions. Most preferred surfactants include, but are not limited to, stearic acid, linoleic acid, linolenic acid, lauric acid, oleic acid and alkali metal salts of disproportionated rosin. An example of commercially available oleic acid is Industrene™ 105 available from Humko Chemical. An example of an alkali metal salt of disproportionated rosin is commercially available from Hercules, Inc. as Dresenate™ 214, which is a potassium salt of predominantly abietic acid. Surfactants that have an HLB of about 15 or greater are preferred, and those with an HLB of about 18 or greater are more preferred.

The amount of dispersing agent needed is very small and depends on the nature and characteristic properties of the tackifier employed. The dispersing agent is present in an amount sufficient to emulsify the tackifier(s). Any concentration of the dispersing agent above the critical micelle concentration can be used in the dispersion. However, if the concentration of the dispersing agent used to prepare the dispersion is too high, preforms or composite parts prepared from the aqueous dispersions may not have the required mechanical properties, since the dispersing agent will remain in the preforms and composites. The term "critical micelle concentration" means the concentration of dispersing agent above which it phase separates from the aqueous solution to form micelles. In general, the dispersing agent is present in an amount of at least about 0.1 weight percent, preferably at least about 0.25 weight percent, more preferably at least about 0.5 weight percent and most preferably at least about 1.0 weight percent, based on the weight of the dispersion. In general, the dispersing agent is present in an amount of at most about 4 weight percent, preferably not greater than about 3 weight percent, more preferably not greater than about 2 weight percent and most preferably not greater than about 1.5 weight percent, based on the weight of the dispersion.

The amount of tackifier applied to the substrate should be sufficient to hold the fibers in the desired shape and position but small enough to leave the resulting preform porous so that it can be readily impregnated with matrix resin during subsequent molding processes. Generally, the tackifier is applied in an amount, on a solids basis, of at least about 0.001 weight percent, preferably at least about 0.25 weight percent, more preferably at least about 1 weight

percent and most preferably at least about 3 weight percent, based on the weight of the reinforcement fibers. Generally, the tackifier is applied in an amount, on a solids basis, of not greater than about 15 weight percent, preferably not greater than about 13 weight percent, more preferably not greater than about 11 weight percent and most preferably not greater than about 10 weight percent, based on the weight of the reinforcement fibers.

The aqueous tackifier dispersion may be applied to the reinforcement fibers by known techniques such as dip coating, nip coating, spray coating, brush coating, kiss rolls, trailing blade, flexographic, inverted knife, polishing bar, wire-wound doctor, direct gravure, offset gravure, two-roll pressure or three-roll pressure.

A typical dip coating method employs a coating set-up which includes a feed spool that supplies the filaments to be coated, a spreading mechanism to separate the fibers into their single fibrils, a coating bath, a drying mechanism and a take-up winder. The spreading mechanism to separate the tows are known and described, for example, in U.S. Patents 5,042,111 and 5,094,883. The spreading mechanism separates multifilament tows into their single filaments or fibrils, so that upon contact with the coating bath, the fibrils are well wet by the dispersion. This would allow the tackifier particles to be deposited on the individual fibrils and obtain a more uniform distribution of the particles on the tow.

Typically, the coating bath is a box containing a few sets of rollers which guide the fibrils through the coating dispersion. The dispersion in the bath is diluted to control the level of pick-up. As spread fibers go through this bath, the suspended particles get coated onto the single fibrils of the tow. The bath volume and the line speed determine the residence time of the fibers within the bath, which in turn influences the concentration for resin applied on the fibers. During the coating process, the concentration of the solid particles in the bath decreases which requires periodic replenishment of the bath with the dispersion to maintain the bath concentration.

Following the coating bath, well-known means, such as convection oven/heating lamps, provide the energy necessary to drive off water and produce partial melting of the resin particles onto the fibrils. In accordance with the present invention, only partial melting of the resin particles is desired in this section of the set-up. If complete melting of the particles occurs, the individual fibrils would form a completely sintered tow that is stiff and not useful for braiding, weaving or filament winding. On the other hand, partial melting of the particles ensures that the tackifier particles adhere well to the fibrils without causing consolidation of the tow.

The coated reinforcement fibers can be dried to remove the water present by conventional methods such as, for example, air-drying at room temperature or drying in a forced-air oven, infrared heating units or microwave heating units. Preferably, the coated reinforcement fibers are dried to a water content of less than about 5 weight percent, more preferably less than about 4 weight percent, and most preferably less than about 3 weight

percent, based on the weight of the coated reinforcement fibers. When drying at temperatures higher than room temperature, the length of time and temperature conditions must be such that the water is evaporated and the tackifier is partially melted or fused on the reinforcement substrate. It is important that the temperature and length of time of drying is sufficient to partially, but not completely melt the resinous compound. Melting the resinous compound completely will cause the coated reinforcement fibers to become stiff and difficult to process.

The preforms of the present invention can be produced in high volume by filament winding and are, therefore, suitable for use in high volume applications such as, for example, the manufacture of golf club shafts, racket frames, baseball bats, softball bats, ski poles, fishing rods, bicycle tubes, bicycle frames and rims, and other similar reinforced structures.

Filament winding is a well-known process for the fabrication of cylindrical fiber-reinforced parts. Filament winding apparatuses are known and are described, for example, in U.S. Patents 3,310,246; 3,334,824 and 4,145,740. Generally, the process comprises winding a series of continuous resin-impregnated filaments or tows over a rotating mandrel. As used herein, a filament comprises strands of twisted and drawn-out fibers and a tow comprises a group of filaments. The mandrel is a core around which the filaments or tows are wound and is made of metal, plaster, plastic, wood or cardboard. The filaments or tows are applied to the mandrel according to a predetermined relationship using conventional numerically computer-controlled or chain and gear mechanical winding machines. The resin-impregnated filaments or tows are cured on the mandrel. The mandrel is subsequently removed from the wound product or may remain as an integral element of the product. In the construction of the present articles, the mandrel is removed from the wound filament. A detailed description of filament winding is described in the Encyclopedia of Polymer Science and Engineering, Second Edition, Vol. 7, pp. 39-52.

If the tackifier used in coating the reinforcement fibers is in the form of a solution (tackifier dissolved in an organic solvent), the preform is preferably prepared by winding the coated filaments or tows onto a mandrel having the shape of a desired article immediately after coming out of the coating bath, while the coated filaments or tows are still wet (Wet Filament Winding). In this set-up, the filaments or tows are very flexible and can be easily wound onto the mandrel, resulting in closer tolerance, net shape, dimensionally stable and compacted/debulked preforms.

The preforms of the present invention can be used in resin transfer molding in high volume production of articles comprising fiber-reinforced composite materials. Resin transfer molding is described, for example, in Plastics Engineering Handbook of the Society of the Plastics Industry, Inc., Fourth Edition, pp. 220-229. Generally, resin transfer molding comprises placing a preform inside a mold, injecting a matrix resin into the mold wherein the

resin impregnates the preform and then cures to provide a fiber-reinforced composite material. The fiber-reinforced composite material is then removed from the mold.

The following working examples and comparative examples are given to illustrate the invention and should not be construed to limit its scope. Unless otherwise indicated, all parts and percentages are by weight.

The following materials are used in the examples:

Resin A is a diglycidyl ether of bisphenol A having a melting point of 55°C to 60°C, an epoxide equivalent weight of 675 to 750 and is available from The Dow Chemical Company as D.E.R.™ 662 UH epoxy resin.

Resin B is a diglycidyl ether of bisphenol A having a viscosity of 4400 cps to 5600 cps (4.4 to 5.6 Pa-s) at 25°C, an epoxide equivalent weight of 172 to 176 and is commercially available from The Dow Chemical Company as TACTIX™ 123 epoxy resin.

Resin C is a bismaleimide resin blend having a viscosity of 50 cps at 130°C and is commercially available from Cytec as 5250-4RTM.

Resin D is a bismaleimide resin having a viscosity of about 2000 cps at 150°C. This resin is prepared in accordance with the method described in Example 2 of U.S. Patent 5,427,725.

Resin E is a diglycidyl ether of bisphenol A having a melting point of 55°C to 60°C and an epoxide equivalent weight of 675 to 750. It is specially formulated to be used as a tackifier and is available from The Dow Chemical Company as Tactix™ 226 epoxy resin.

Hardener A is a cycloaliphatic diamine having a viscosity of 8 to 12 cps (0.008 to 0.12 Pa-s) at 25°C, an amine equivalent weight of 28 to 29 and is commercially available from Milliken Chemical Company as Millamine™ 5260.

Example 1

A. Preparation of Aqueous Dispersion of Resinous Compound

A 70 weight percent solution of Resin A in toluene was prepared. An aqueous dispersion containing 46 weight percent tackifier was prepared from this solution. The dispersing agent used was Alipal™ CO-436 sulfated nonylphenoxy poly(ethyleneoxy) ethanol at 2.5 percent by weight based on Resin A. The solvent was removed and the dispersion was concentrated to 58 percent solids by weight. The resulting dispersion contained resin particles having an average diameter of 0.64 µm and was easily dilutable with water to provide lower tackifier concentrations for control of coating operations.

B. Preparation of Preforms

Graphite fabric AW370-8H (Hercules, Inc., Magna, UT) with epoxy sizing was cut into 10 by 12 inch (25.4 by 30.48 cm) pieces. Using a spray bottle, the graphite pieces (plies) are spray-coated on one side with the aqueous dispersion prepared in Part A to deposit onto the

plies from 4 to 4.5 weight percent Resin A, based on the weight of the fabrics. The individual coated plies are dried for 30 minutes at room temperature, further dried in an oven at 110°C (230°F) for 30 minutes and cooled to room temperature. A visual examination of the dried coated plies reveals a substantially uniformly distributed discontinuous film coating of the tackifier on their surfaces. To prepare an eight-ply preform, eight of the coated pieces were stacked, aligned and prepared for debulking. Debulking was done by vacuum bagging. The stacked pieces were placed on a baseplate covered with tetrafluoroethylene film. Felt was placed around the fabric leading to a vacuum port and covered with a bag material. The whole assembly was placed under a vacuum of 30-inch Hg and heated to 93°C (199°F) and maintained at this temperature for 30 minutes. The assembly was allowed to cool to room temperature under vacuum and the finished eight-ply preform was removed from the vacuum bag.

Example 2 Preparation of Three-Dimensional Preforms

Following the procedure of Part A of Example 1, an aqueous dispersion of Resin A having a 29.1 percent solids concentration was prepared. Eight mats of graphite fabric AW370-8H (Hercules, Inc., Magna, UT) were coated with the aqueous dispersion using an air brush. Three to five weight percent of Resin A, based on the weight of the fabric, was deposited on the mats. The coated mats were allowed to air-dry at room temperature for 2 hours. A visual examination of the dried coated mats revealed a substantially uniformly distributed discontinuous film coating of the tackifier on the mat surfaces. After air-drying, the mats were cut into 6 by 8.5 inch (15.24 by 21.6 cm) pieces. Eight pieces were laid on top of each other, aligned and placed on a mold to obtain a C-shaped preform. The whole assembly was prepared for vacuum bagging following the procedure of Example 1. Vacuum bagging was performed at 95°C (203°F) for 90 minutes. The assembly was cooled to room temperature maintaining a 30-inch Hg vacuum. The three-dimensional preform was then removed from the vacuum bag.

Comparative Example A Preparation of Control Preforms

Graphite fabric AW370-8H (Hercules, Inc., Magna, UT) with epoxy sizing was cut into 10 by 12 inch (25.4 by 30.48 cm) rectangles. Eight layers of fabric were stacked, aligned and debulked following the procedure described in Example 1.

Comparative Example B Preparation of Powder Coated Preforms

Graphite fabric AW370-8H (Hercules, Inc., Magna, UT) with epoxy sizing was cut into 10 by 12 inch (25.4 by 30.48 cm) rectangles. Resin A ground to 100 mesh powder, as described in U.S. Patent 4,992,228, was evenly sprinkled on seven of the fabric plies using a 100 mesh sieve. The seven coated plies were stacked and aligned. An eighth-ply (not coated) was placed on top of the assembly. The amount of tackifier employed was 4.2 percent by weight of graphite fabric. The assembly was debulked following the procedure described in Example 1.

Example 3A. Preparation of Composite Panel

The preforms prepared in Example 1 and Comparative Examples A and B were placed in a mold cavity and the mold was heated to a temperature of from 60°C to 65°C (140°F to 150°F). Resin B and Hardener A are mixed at 35°C to 40°C (90°F to 110°F) and the resulting resin formulation was introduced into the mold cavity at this temperature under a back pressure of 50 psi. After 10 minutes, the back pressure was increased to 90 psi. The injection period was 30 minutes. The mold temperature was raised to 177°C (350°F) at a rate of about 3°C/minute (6°F/minute). The mold temperature was held at 177°C for 30 minutes and lowered to 40°C (104°F) at a rate of about 3°C/minute (6°F/minute). After molding, all panels were simultaneously post-cured for 120 minutes at 177°C (350°F).

B. Conditioning of Composite Sample

The composite samples which were to be tested wet for mechanical properties were first dried for three days at 80°C (176°F). They were then placed in boiling water for two weeks and tested immediately upon their removal.

The compressive test specimens required tabs which measured 5.72 cm (2.25 inches) long by the width of the sample. Tabs were adhered to both sides of the samples at both ends with American Cyanamid's FM123-2 adhesive film, an epoxy resin which required a cure of one hour at 100°C (212°F). Tabs were made from G-10FR grade epoxy resin/glass sheet, 0.157 cm (0.062 inches) thick, obtained from Norplex-Oak Company.

C. Testing of Composite Panel

The mechanical properties of the composite panels were determined using an Instron Model 1127 tensile testing machine with a 50,000 pound load cell. The short beam shear tests were conducted following ASTM DD-2344. The compressive tests were performed following ASTM D-3410, the IITRI compressive test procedure. The test results are shown in Table I. Values in parentheses represent the standard deviation of the measurements.

30

35

Table I

Compressive and Short Beam Shear Results

<u>Composite Description</u>		<u>Short Beam Shear Strength</u>	<u>Compressive Strength</u>
Control, no binder	dry	8.81 (0.22) (ksi) 61 (1.5) (MPa)	67.4 (8.4) (ksi) 467 (58) (MPa)
	wet	8.10 (0.18) (ksi) 56 (1.2) (MPa)	61.4 (4.5) (ksi) 423 (31) (MPa)
Aqueous dispersion coated preform, 4.17% by weight	dry	9.03 (0.35) (ksi) 62.3 (2.4) (MPa)	58.8 (3.4) (ksi) 406 (23) (MPa)
	wet	8.41 (0.25) (ksi) 58 (1.7) (MPa)	60.5 (7.3) (ksi) 417 (50) (MPa)
Powder coated preform, 4.2% by weight	dry	6.92 (0.93) (ksi) 48 (6.4) (MPa)	54.8 (5.4) (ksi) 378 (37) (MPa)
	wet	6.62 (0.98) (ksi) 46 (6.7) (MPa)	50.8 (2.8) (ksi) 350 (19) (MPa)

The data in the above table show that there was better retention of composite properties on parts made from preforms prepared with the aqueous tackifier dispersions of the present invention.

20 Example 4 Preparation of Aqueous Dispersion Coated Preforms

Graphite fabric AW370-8H (Hercules, Inc. Magna, UT) with epoxy sizing was cut into 2 inch by 3 inch (5.08 cm by 7.62 cm) rectangles (mats). An aqueous dispersion of Resin C was prepared as in Example 1. The dispersion had 44 percent solids concentration and average particle diameter of 0.7 μm . The dispersion was sprayed on two mats by means of a spray bottle to obtain a tackifier concentration of approximately 13 percent by weight of graphite fabric. Once sprayed, the individual mats were air-dried for 30 minutes at room temperature. The coated mats were stacked, aligned and debulked following the procedure described in Example 1. The resulting preform showed high rigidity and adhesion between the plies.

25 Example 5 Preparation of Aqueous Dispersion Coated Preforms

Graphite fabric AW370-8H (Hercules, Inc. Magna, UT) with epoxy sizing was cut into 2 in. x 3 in. (5.08 cm x 7.62 cm) rectangles (mats). An aqueous dispersion of Resin D was prepared as in Example 1. The dispersion has 30 percent solids concentration and average particle diameter of 1.2 μm . The dispersion was sprayed on two mats by means of a spray bottle to obtain a tackifier concentration of approximately 13 percent by weight of graphite fabric. Once sprayed, the individual mats were air-dried for 30 minutes at room temperature. The coated mats were stacked, aligned and debulked following the procedure described in Example 1. The resulting preform showed high rigidity and adhesion between the plies.

Example 6A. Coating of Tows

The set-up utilized to perform tow coating was as described previously. The tow utilized was unsized IM7-12K tow from Hercules Inc. An aqueous dispersion of Resin A was prepared as in Example 1. The dispersion had 58.2 percent solids content with an average particle size of approximately 0.6 micrometers. A 24:1 dilution ratio was used to obtain the appropriate resin concentration on the fibers. At line speeds of approximately 2 cm/second, a concentration of Resin A of 3 to 5 percent by weight of uncoated fibers were deposited on the tows. The coated tow obtained had the flexibility and handling characteristics of the uncoated tow. This would allow further processing such as weaving, braiding and filament winding. The resin particles were uniformly distributed on the individual fibrils. The average particle size was smaller than the fiber diameter and the particles partially melted on the fibrils.

B. Consolidation of Coated Tow

IM7-12K tow coated as described in Part A of this example was heated to approximately 110°C for a few minutes and allowed to cool down to room temperature. The resulting tow was rigid and stiff, having the consistency and stiffness of a graphite lead. This showed the ability of the coated tow to form a rigid preform useful for resin transfer molding.

Example 7 Filament Winding with Resin E/Methylene Chloride Solution

An 8 percent solution was utilized for impregnating a continuous strand of Amoco T250 12k fiber. The tow was dragged through a conventional resin bath after passing over a single breaker bar. The tow was drawn through the bath while passing under a kiss roll. The tow was immediately wound on a mandrel of approximately 0.500-inch diameter using a hoop wind, which was a filament winding technique using a constant high angle (typically about 87 degrees). Four plies/layers are wound to a length of 3 to 4 inches. The wound tube on the mandrel was placed in a convection oven for 20 minutes at a temperature of 100°C. The solids content of the dry fiber was 13.3 percent by weight of graphite.

Example 8 Filament Winding with Aqueous Dispersion of Resin A

A 20 percent solids content dispersion was diluted to 10 percent with deionized water and processed by the same method and materials described above. The 10 percent solids content of the dry fiber was 9.3 percent by weight of graphite.

Example 9 Filament Winding with Resin E/Acetone Solution

A 4 percent solution was used for impregnation of shafts 1 through 3 as described in the following Filament Winding methods.

Example 10 Filament Winding with Aqueous Dispersion of Resin A

A 20 percent solids content dispersion was diluted with deionized water to 4.4 percent and used for impregnation of shafts 4 through 6 as described in the following Filament Winding methods.

Filament Winding Methods

A single spool of Amoco T250 12k was loaded into the CTC tension units and the tension adjusted to 4 pounds. The letters "CTC" refers to a constant tension control device that maintained constant balanced tension on the fibers as they exited the spool. Parts were then wound dry to establish a pattern and determine possible wall thickness. A linear 20-degree program was selected. This resulted in a 20-degree wind angle on the butt and a 5.7-degree wind angle at the tip. It was determined that a 2-circuit/pattern program with a fiber band width of 18 inches yielded the smoothest finish and best consistency. Layer thickness was 0.025 inches to 0.028 inches on the butt end. The helical winding program was shown in

Table II:

Table II

	H ¹ = 5"	L ⁴ = 58.8"
	Range ² = 3"	Range mode = linear
	Angle = 20°	Band width = 18"
	Mandrel dia = 0.51"	Lead or Lag = Lead
	Circuit/Pattern = 2	Circuit/Core = 2
	Dwell ³ = 1.3"	End Revolutions = 4.01894
Revolutions/Circuit = 29.778		

¹Location of headstock

²Turn-around area of the filament-wound part

³Dwell turn-around

⁴Winding length

The mandrel was chucked 1.5 inches on the butt and 1 inch on the tip end. Actual winding started at 5.75 inches on the butt and ends 3.75 inches from the tip. Tackifier was then added to the resin bath and the first part wound. After winding the first part, it was determined that the tip was undersized and an additional layer was needed to be added to just the tip section. The following circumferential wind program was added between the first and second layer.

	<u>Section 1</u>	<u>Section 2</u>
	Carriage start = 5"	Carriage start = 40"
	Carriage stop = 40"	Carriage stop = 59"
5	Angle = 46.321°	Angle = 70.1517°
	Band width = 6"	Band width = 0.16"
	Mandrel diameter = 2"	Mandrel diameter = 0.150 "

Following are the outside diameter measurements of the six wound parts and the
10 wind tension used:

	<u>Part 1</u>	<u>Part 2</u>	<u>Part 3</u>	<u>Part 4</u>	<u>Part 5</u>	<u>Part 6</u>
	<u>Butt, in</u>	<u>Butt, in</u>	<u>Butt, in</u>	<u>Butt, in</u>	<u>Butt, in</u>	<u>Butt, in</u>
15	0.598	0.593	0.590	0.593	0.594	0.591
	0.599	0.599	0.584	0.592	0.588	0.593
	0.595	0.592	0.586	0.597	0.592	0.592
	<u>Tip, in</u>	<u>Tip, in</u>	<u>Tip, in</u>	<u>Tip, in</u>	<u>Tip, in</u>	<u>Tip, in</u>
	0.303	0.308	0.319	0.325	0.327	0.326
	0.305	0.309	0.316	0.320	0.324	0.316
20	T = 4 lbs	T = 5 lbs	T = 4 lbs	T = 4 lbs	T = 4 lbs	T = 4 lbs

Using parts 2 through 6, the butt-end diameter varied from 0.588 inches to
25 0.599 inches (or 0.11") and the tip end varied from 0.308 inches to 0.326 inches (or 0.18 inches).
Maximum variation within the shafts was 0.007 inches butt end, and 0.010 inches tip end.
Weight appeared to remain constant at 72.5 grams. The fiber speed was varied from
17.5 ft/minute to 21.5 ft/minute with no noticeable change in dimensions. Tension of the fiber
appeared to make the largest change in the dimensions on the tip end, but had little effect on
30 the butt end. These data demonstrated an ability to manufacture close tolerance, net shape,
dimensionally stable preforms for Resin Transfer Molding (RTM), utilizing automated high rate
fiber placement techniques, such as filament winding. This allowed for a cost-effective
approach for RTM manufacture in high volume applications.

35

CLAIMS:

1. A process for preparing preforms which comprises the sequential steps of
(1) coating reinforcement fibers, in the form of continuous filaments or tows, with an aqueous
dispersion of a tackifier, (2) winding the coated filaments or tows, while still wet, onto a
mandrel having the shape of a desired article, (3) heating the coated reinforcement fibers to a
temperature and for a time sufficient to remove the water present and to partially melt the
tackifier on the surface of the reinforcement fibers and (4) removing the mandrel from the
wound reinforcement fibers to provide a preform.
2. The process of Claim 1 wherein the tackifier is an epoxy resin, a vinyl ester
resin, unsaturated polyester resin, polycyanate ester resin, benzocyclobutene resin, polyimide,
bismaleimide, or mixtures thereof.
3. The process of Claim 2 wherein the epoxy resin is a diglycidyl ether of biphenol,
bisphenol, hydrocarbyl-substituted biphenol, hydrocarbyl-substituted bisphenol, phenol- or
hydrocarbyl-substituted bisphenol-aldehyde novolac resin, unsaturated hydrocarbon-phenol
or hydrocarbyl-substituted phenol resin.
4. The process of Claim 3 wherein the epoxy resin is a diglycidyl ether of
bisphenol A having an epoxide equivalent weight of from 650 to 750.
5. The process of Claim 2 wherein the bismaleimide is 4,4'-
bismaleimidodiphenylmethane or 1,4-bismaleimido-2-methylbenzene, a modified
bismaleimide containing Diels-Alder comonomers, a partially advanced modified bismaleimide
containing Diels-Alder comonomers, or a partially advanced bismaleimide based on 4,4'-
bismaleimidodiphenylmethane and allylphenyl compounds or aromatic amines; the vinyl ester
resin is the reaction product of bisphenol A and acrylic acid and has a number average
molecular weight of from 950 to 1250; and the unsaturated polyester resin is the reaction
product of fumaric acid and propoxylated or ethoxylated bisphenol A, the reaction product of
maleic anhydride and ethoxylated or propoxylated bisphenol A, or the pentaerythritol ester of
tall oil resin.
6. The process of Claim 1 wherein the aqueous dispersion has a resin solids
content of at least 0.1 weight percent, based on the weight of the dispersion.
7. The process of Claim 1 wherein the aqueous dispersion has a resin solids
content of at least 29 weight percent, based on the weight of the dispersion.
8. The process of Claim 1 wherein the aqueous dispersion has a resin solids
content of not greater than 70 weight percent, based on the weight of the dispersion.
9. The process of Claim 1 wherein the tackifier is applied to the reinforcement
fiber in an amount of at least 0.001 weight percent and not greater than 15 weight percent,
based on the weight of the reinforcement fibers.

10. The process of Claim 1 which further comprises the step of debulking the shaped, coated reinforcement fibers.

11. The process of Claim 1 wherein the reinforcement fiber is in the form of a woven or non-woven mat.

5 12. A process for preparing preforms which comprises the sequential steps of (1) coating reinforcement fibers, in the form of continuous filaments or tows, with a tackifier dissolved in an organic solvent, (2) winding the coated filaments or tows, while still wet, onto a mandrel having the shape of a desired article, (3) heating the coated reinforcement fibers to a temperature and for a time sufficient to evaporate the solvent and to melt the tackifier on the
10 surface of the reinforcement fibers and (4) removing the mandrel from the wound reinforcement fibers to provide a preform.

 13. A process for preparing preforms which comprises the sequential steps of (1) coating reinforcement fibers, in the form of continuous filaments or tows, with an aqueous dispersion of a tackifier, (2) heating the coated reinforcement fibers to a temperature and for a
15 time sufficient to remove the water present and to partially melt the tackifier on the surface of the reinforcement fibers, (3) winding the coated filaments or tows onto a mandrel having the shape of a desired article and (4) removing the mandrel from the wound reinforcement fibers to provide a preform.

 14. A process for making an article made of a fiber-reinforced composite material
20 which comprises:

 (1) preparing a preform by (i) coating reinforcement fibers with an aqueous dispersion of a tackifier, (ii) forming the coated reinforcement fibers into a preform having the shape of a desired article and (iii) heating the coated reinforcement fibers to a temperature and for a time sufficient to remove the water present and to partially melt the tackifier on the
25 surface of the reinforcement fibers; and

 (2) subjecting the preform to a resin transfer molding process to provide an article comprising a fiber-reinforced composite material.

 15. The process of Claim 14 wherein the article is a golf club shaft, racket frame, baseball bat, softball bat, ski pole, fishing rod, bicycle tube, bicycle frame or bicycle rim.

30 16. The process of Claim 15 wherein the article is a golf club shaft.

 17. A process for making an article made of a fiber-reinforced composite material which comprises:

 (1) preparing a preform by (i) coating one or more reinforcement fibers in the form of a continuous filament or tow with an aqueous dispersion of a tackifier, (ii) winding the
35 coated filament or tow, while still wet, onto a mandrel having the shape of a desired article, (iii) heating the coated reinforcement fibers to a temperature and for a time sufficient to remove the water present and to partially melt the tackifier on the surface of the

reinforcement fibers and (iv) removing the mandrel from the filament-wound reinforcement fibers to provide a preform; and

(2) subjecting the preform to a resin transfer molding process to provide an article comprising a fiber-reinforced composite material.

5 18. The process of Claim 17 wherein the article is a golf club shaft, racket frame, baseball bat, softball bat, ski pole, fishing rod, bicycle tube, bicycle frame or bicycle rim.

19. The process of Claim 18 wherein the article is a golf club shaft.

20. A process for making an article made of a fiber-reinforced composite material which comprises:

10 (1) preparing a preform by (i) coating one or more reinforcement fibers in the form of a continuous filament or tow with a tackifier dissolved in an organic solvent, (ii) winding the coated filament or tow, while still wet, onto a mandrel having the shape of a desired article, (iii) heating the coated reinforcement fibers to a temperature and for a time sufficient to evaporate the solvent and to melt the tackifier on the surface of the reinforcement
15 fibers and (iv) removing the mandrel from the filament-wound reinforcement fibers to provide a preform; and

(2) subjecting the preform to a resin transfer molding process to provide an article comprising a fiber-reinforced composite material.

20 21. The process of Claim 20 wherein the article is a golf club shaft, racket frame, baseball bat, softball bat, ski pole, fishing rod, bicycle tube, bicycle frame or bicycle rim.

22. The process of Claim 21 wherein the article is a golf club shaft.

23. A process for preparing an article made of a fiber-reinforced composite material which comprises:

25 (1) preparing a preform by (i) coating reinforcement fibers in the form of continuous filaments or tows with an aqueous dispersion of a tackifier, (ii) drying the coated reinforcement fibers for a time and temperature sufficient to remove the water present and to partially melt the tackifier on the surface of the reinforcement fibers, (iii) applying the coated reinforcement fibers by filament-winding onto a mandrel having the shape of a desired article and (iv) removing the mandrel from the filament-wound reinforcement fibers to provide a
30 preform; and

(2) subjecting the preform to a resin transfer molding process to provide an article comprising a fiber-reinforced composite material.

24. A preform comprising reinforcement fibers having a substantially uniformly distributed tackifier on the surface thereof in the form of a discontinuous film coating.

35 25. A preform prepared by the process of Claim 1.

26. A preform prepared by the process of Claim 2.

27. An article prepared by the process of Claim 17.

28. An article prepared by the process of Claim 20.

29. A preform comprising reinforcement fibers having a substantially uniformly distributed tackifier on the surface thereof in the form of a discontinuous film coating.

30. A preform prepared by (1) applying an aqueous dispersion of a tackifier onto one or more reinforcement fibers, (2) drying the coated reinforcement fibers to remove the water present and (3) forming one or more of the coated reinforcement fibers into a predetermined shape.

31. The preform of Claim 19 wherein the fiber is in the form of a woven or non-woven mat.

32. A preform prepared by (1) applying an aqueous dispersion of a tackifier onto one or more reinforcement fibers in the form of continuous filaments or tows, (2) heating the coated reinforcement fibers to a temperature sufficient to partially melt the tackifier on the surface of the reinforcement fibers, (3) drying the coated reinforcement fibers to remove the water present and (4) heating the dried coated reinforcement fibers to a temperature sufficient to produce a rigid preform.

33. A fiber-reinforced composite comprising the preform of Claim 29.

34. A fiber-reinforced composite comprising the preform of Claim 30.

35. A fiber-reinforced composite comprising the preform of Claim 31.

36. A fiber-reinforced composite comprising the preform of Claim 32.

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.
PCT/US 97/00898

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29B11/16 B29B15/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 32085 A (DOW CHEMICAL CO) 30 November 1995 see page 6, line 35 - page 7, line 17; claims 13-16 ---	1-11,13, 14,17, 23-30, 32-34,36
X	EP 0 547 330 A (SUMITOMO RUBBER IND) 23 June 1993 see page 5, line 14 - line 22 -----	12,20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *A* document member of the same patent family

Date of the actual completion of the international search

3 September 1997

Date of mailing of the international search report

15.09.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Van Wallene, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/US 97/00898

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9532085 A	30-11-95	US 5480603 A EP 0759842 A US 5593758 A	02-01-96 05-03-97 14-01-97
EP 0547330 A	23-06-93	JP 5208427 A JP 5104571 A JP 8018346 B	20-08-93 27-04-93 28-02-96